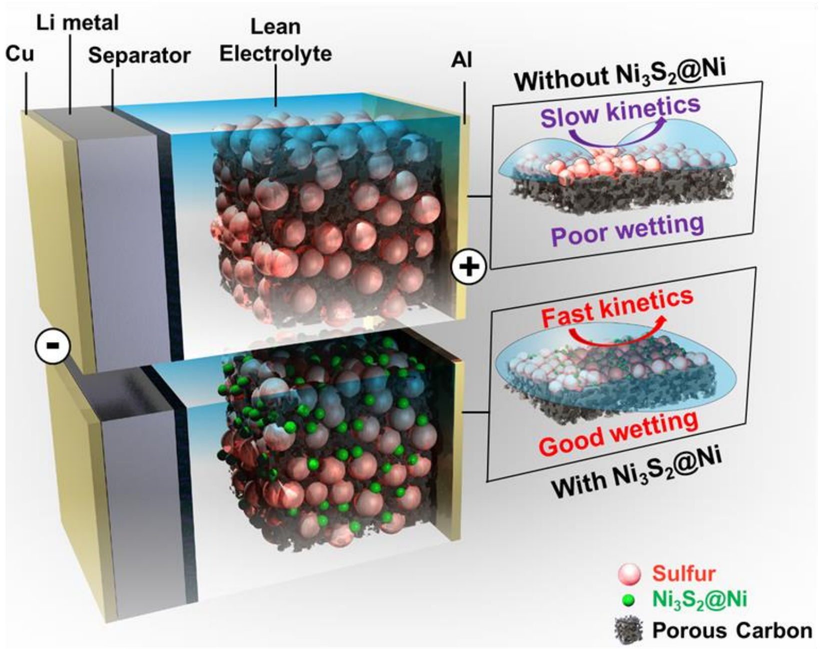
Bat368: Battery500 Integrated Cell Diagnostics and Modeling to Identify Critical Gaps in Achieving High Cycle Life



ERIC DUFEK
Idaho National Laboratory

Contributors:
INL, PNNL, UCSD, BNL, SUNY Binghamton, SLAC, University of Washington, UT-Austin, NCSU, Princeton

June 2, 2020
Web Conference

INL/MIS-20-58161

Overview

Timeline

- **Start: October 1, 2016**
- **End: September 30, 2021**
- **Percent Complete: 70%**

Barriers

- Complex design considerations and aging profiles
- Alignment of mechanical and electrochemical responses
- Low energy density and high cost of fast charge cells
- As energy increases need for safe operation is imperative

Budget

- Total project funding: DOE share $50M
- Funding received in FY 2019: $10M
- Funding for FY 2020: $10M

Partners

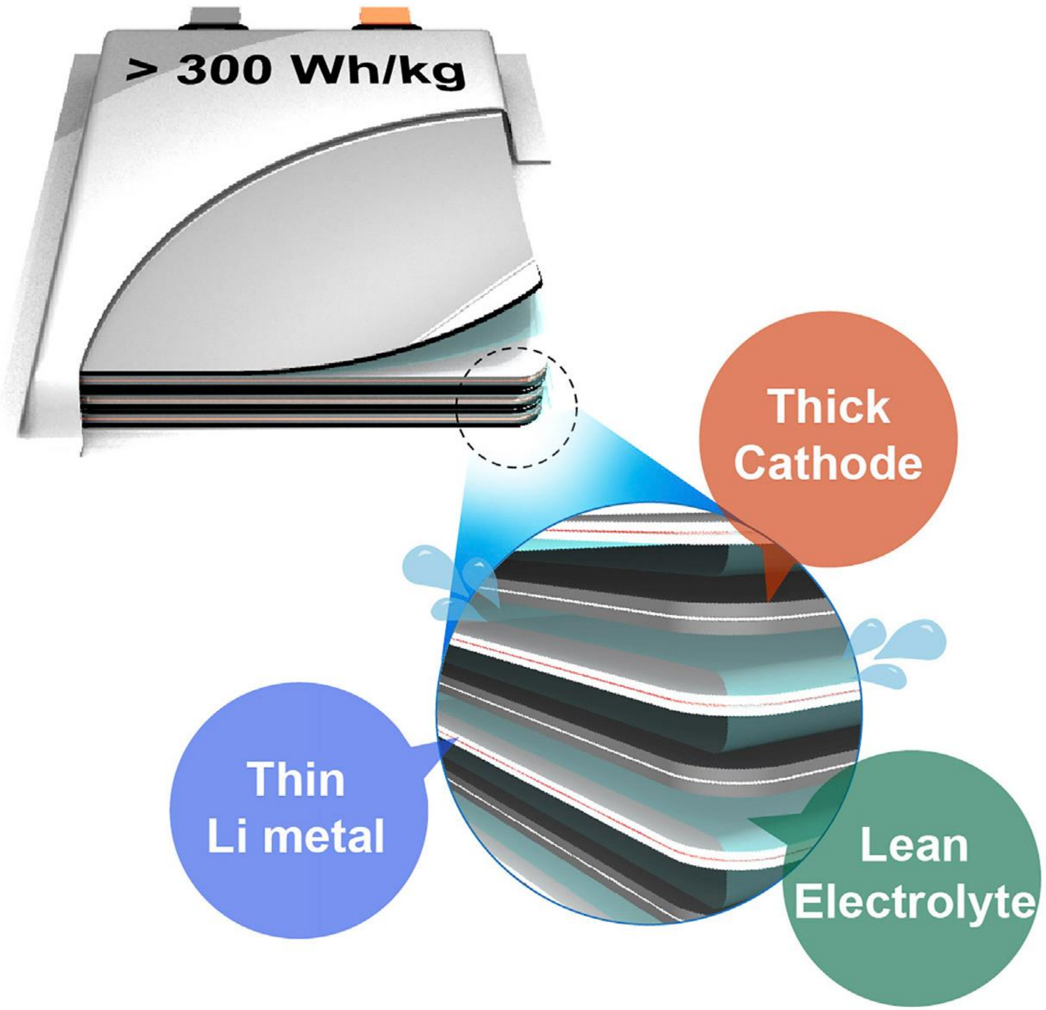
- Pacific Northwest National Laboratory, Idaho National Laboratory, Brookhaven National Laboratory, Stanford Linear Accelerator National Laboratory, Stanford University, University of Washington, University of Texas-Austin, UC San Diego, SUNY Binghamton

Relevance

Advancing ability to develop safe, high energy batteries

Integrating technologies and materials can be tricky and create secondary failure mechanisms

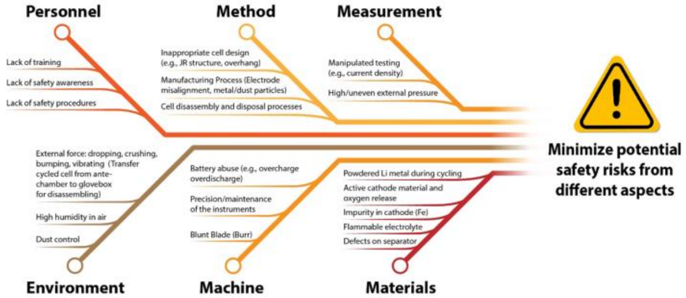
Optimization of cell parameters is vital to both create high energy systems and drive advancement within the community



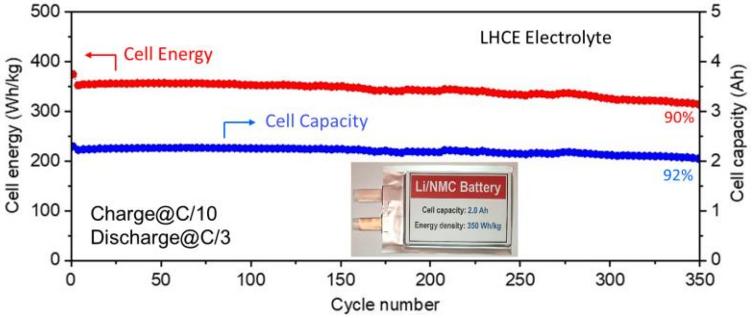
S. Chen et al, Joule, **2019**, 3, 1-12

Approach and Milestones

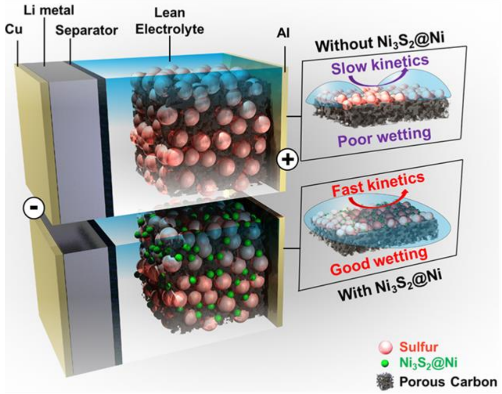
Safety



Life impacts for Li/NMC

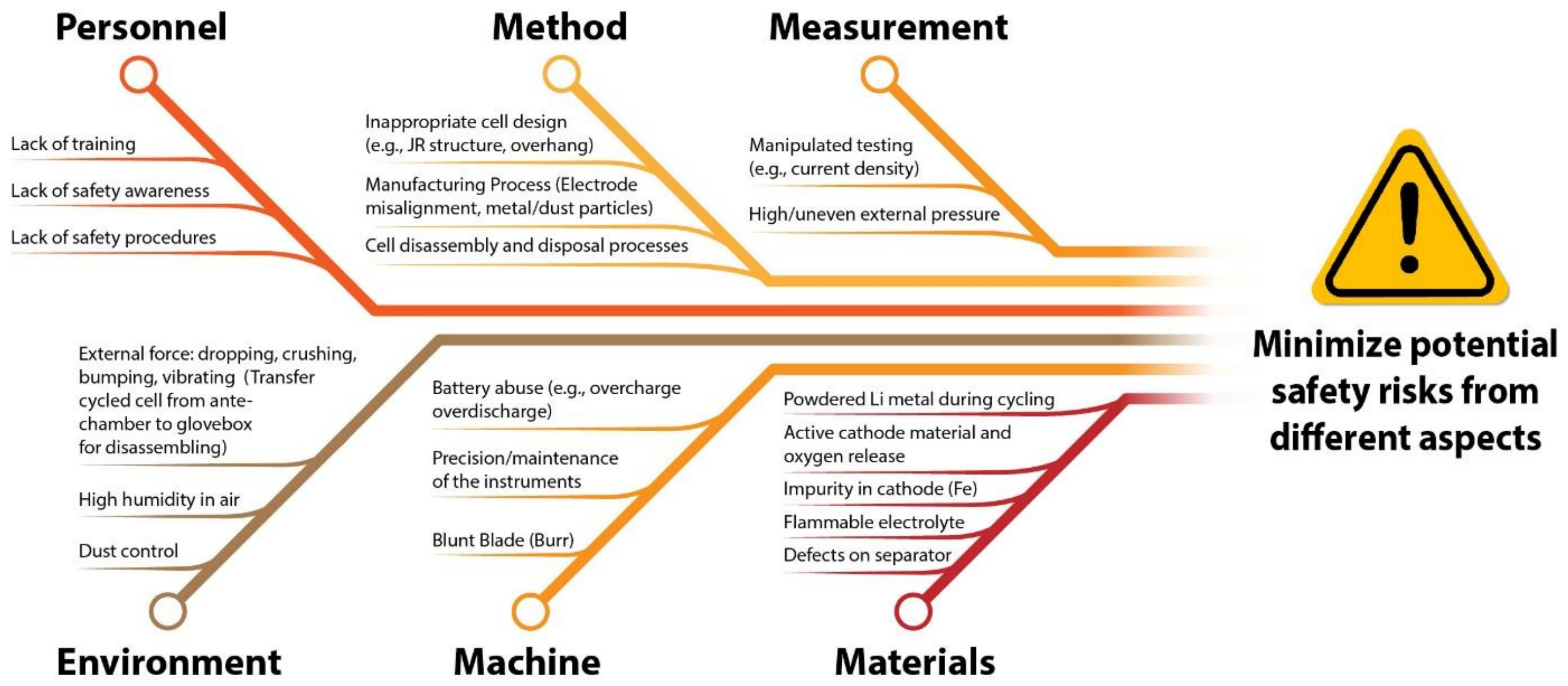


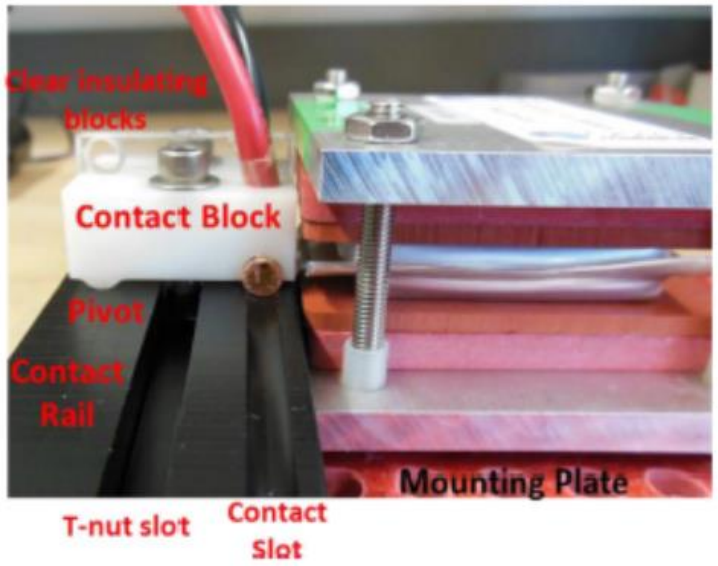
Life and design impacts for Li-S



Milestone	Quarter	Status
Develop methods to enhance understanding of cell failure for Li/NMC	Q1 (12/31/19)	Complete
Quantify different aging for calendar and cycle life cells (Li/NMC)	Q2 (3/31/20)	Complete
Provide guidance on impact of cycling use scenarios on cell cycle life	Q3 (6/30/20)	In Progress
Expand analysis methods to include both Li-S and Li/NMC	Q4 (9/30/20)	In Progress

Good Practices for Development and Evaluation of Rechargeable Li Metal Batteries

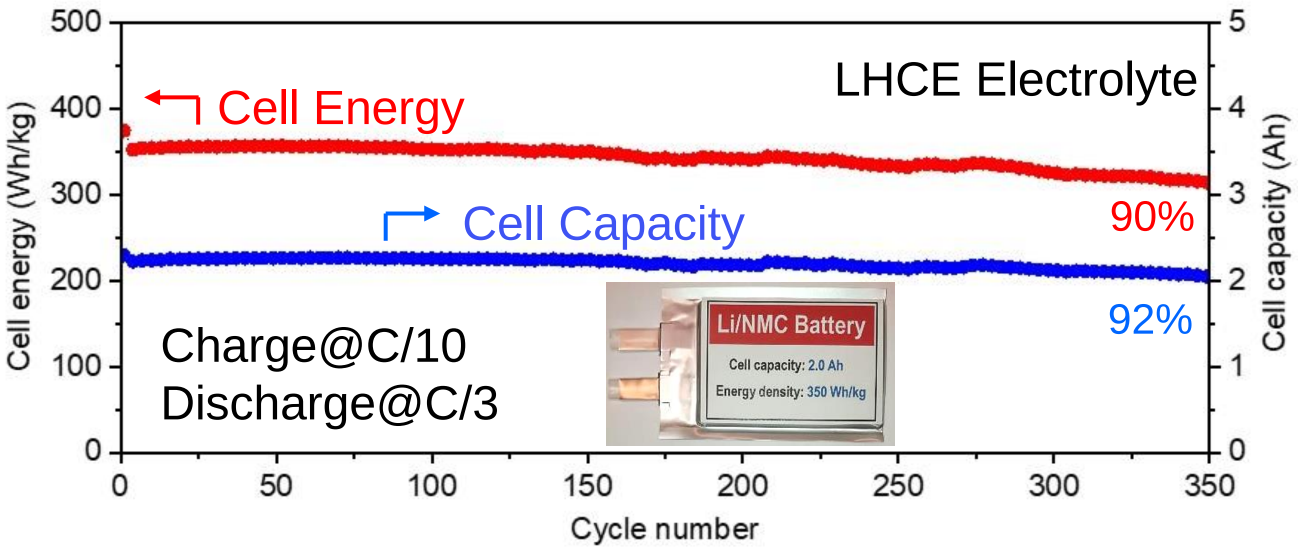


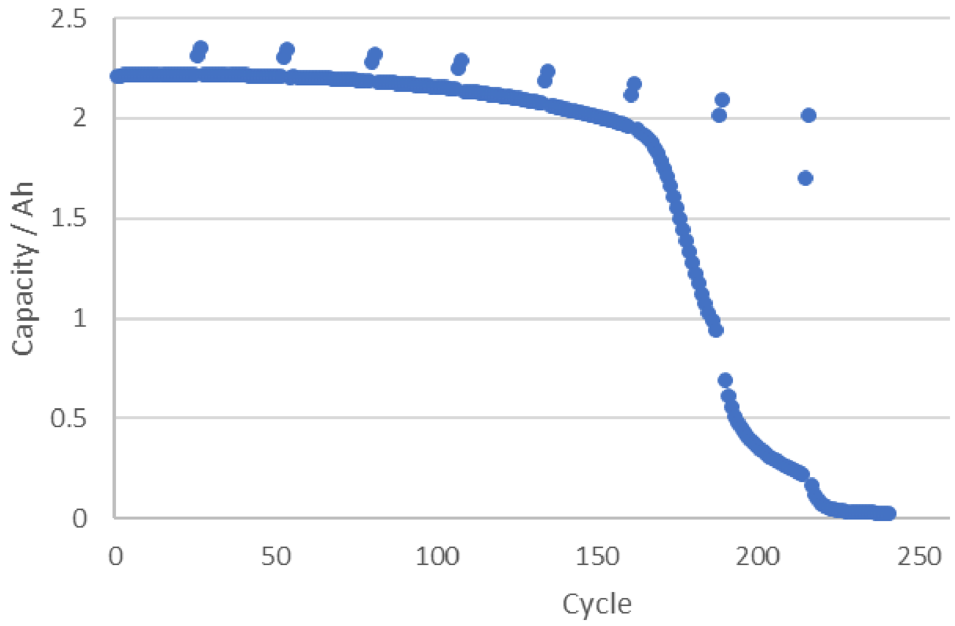


Dissemination of knowledge within the research community

Bewley, R. et al, *J. Electrochem. Soc*, **166**(8), E263 (2019)
Wu, B. et al, *J. Electrochem. Soc*, **166**(16), A4141 (2019)

350 Wh/kg (2.5 Ah) Li Metal Battery for 350 Stable Cycling





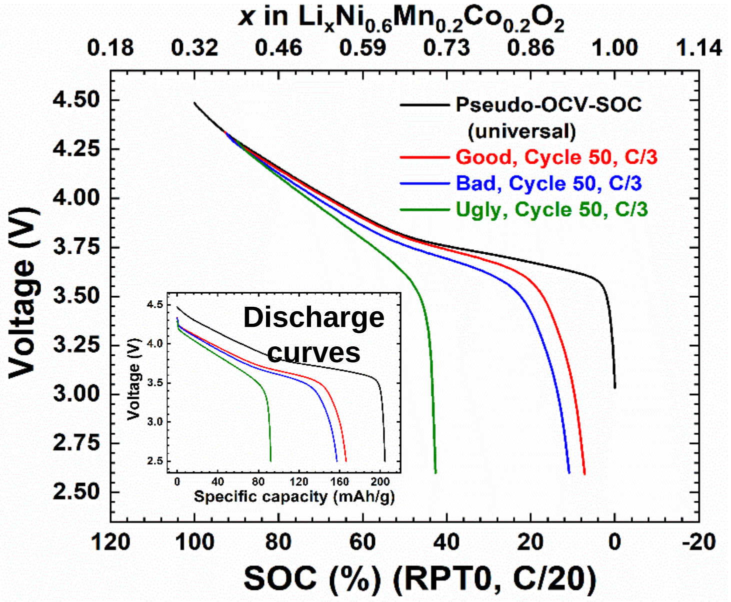
- Multi-site verification of performance
- New electrolyte and design to extend life and enhance specific energy
- Path dependency and variation in rates may impact life
- See Bat369 (Jie Xiao) for more details

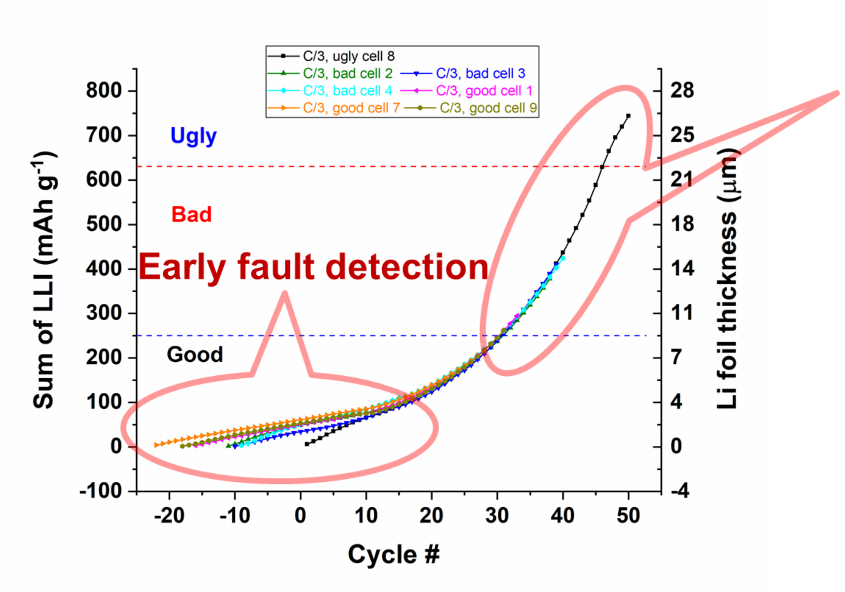
Idaho National Laboratory

Failure Diagnostics to Identify Cell Design & Performance Gaps

- Quantify capacity fade attributes between Li and NMC electrodes, cell-to-cell, cycle-by-cycle

- Complete life cycle analysis to help identify gaps in materials, electrodes, and cell level for specific energy and cycle life

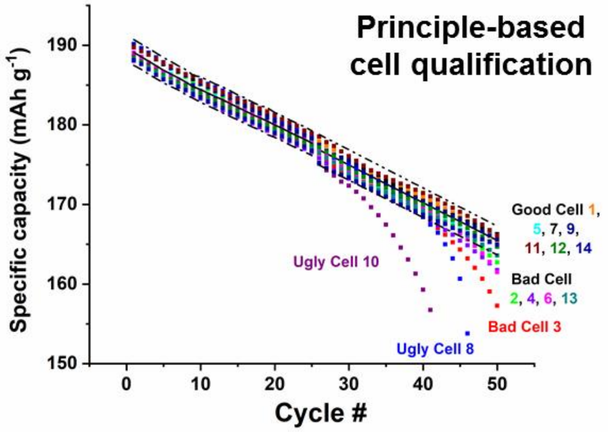




Life prediction

Remaining Useful Life for each cell:

Bad cell 2: 8 cycles
Bad cell 3: 7 cycles
Bad cell 4: 6 cycles
Good cell 1: 13 cycles
Good cell 7: 19 cycles
Good cell 9: 15 cycles



Zhang Y. et al. *J. Electrochem. Soc.* **167**(9), 090502 (2020)

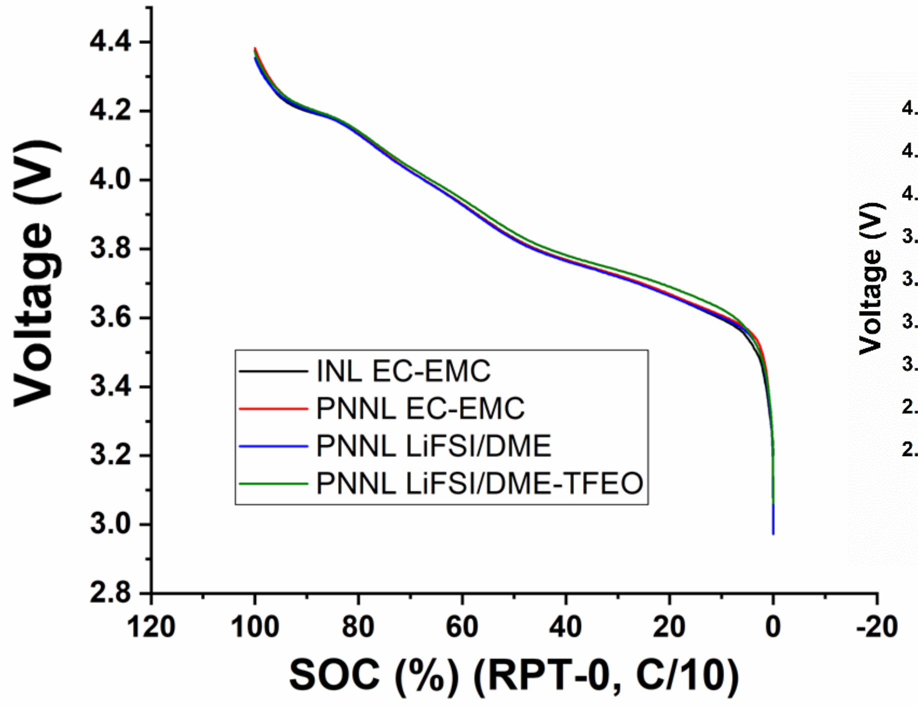
Electrochemical Analytic Diagnosis

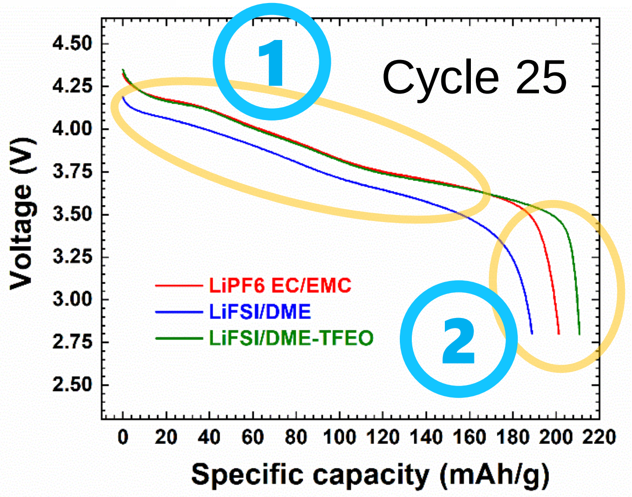
1 Interfacial kinetics

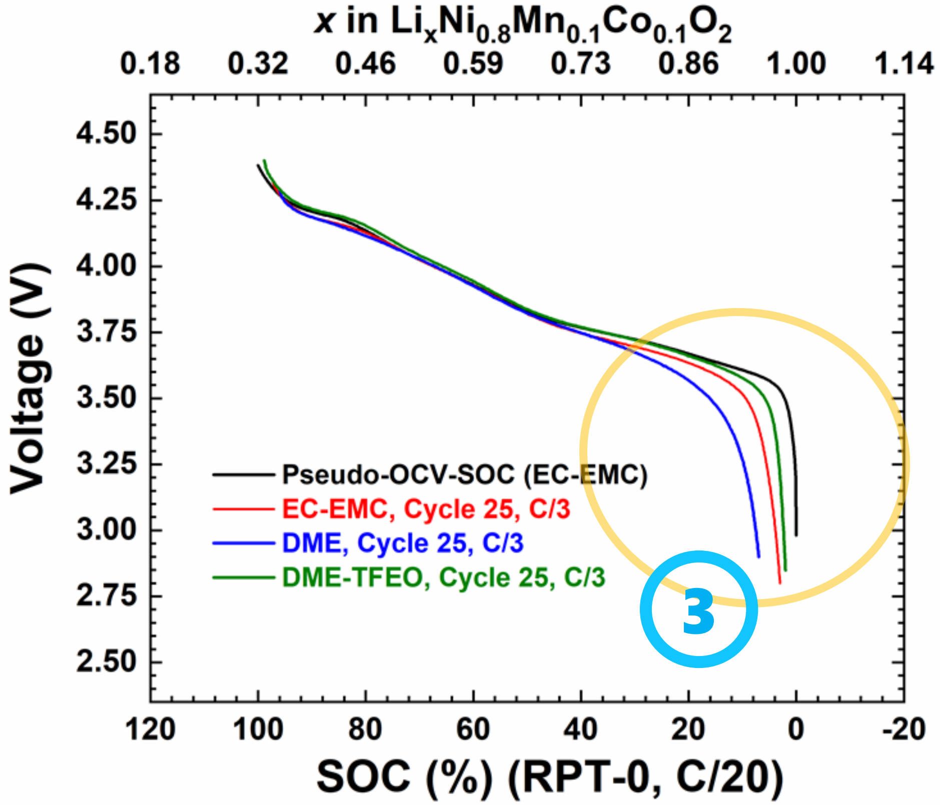
2 Impact of interfacial kinetics on capacity

3 Impact of interfacial kinetics on site occupancy

Pseudo-OCV–SOC curves from 4 Li–NMC-811 cells





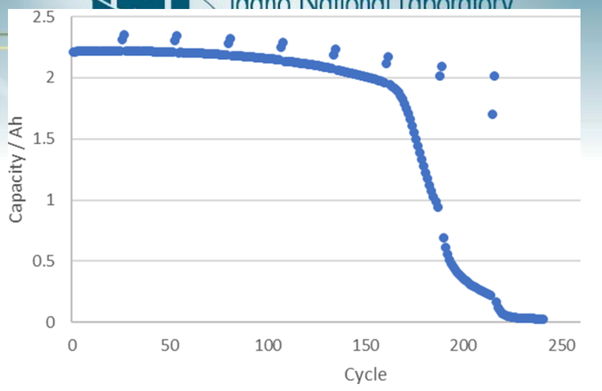


X. Cao et al, *Nature Energy* 4 (2019) 796–805.

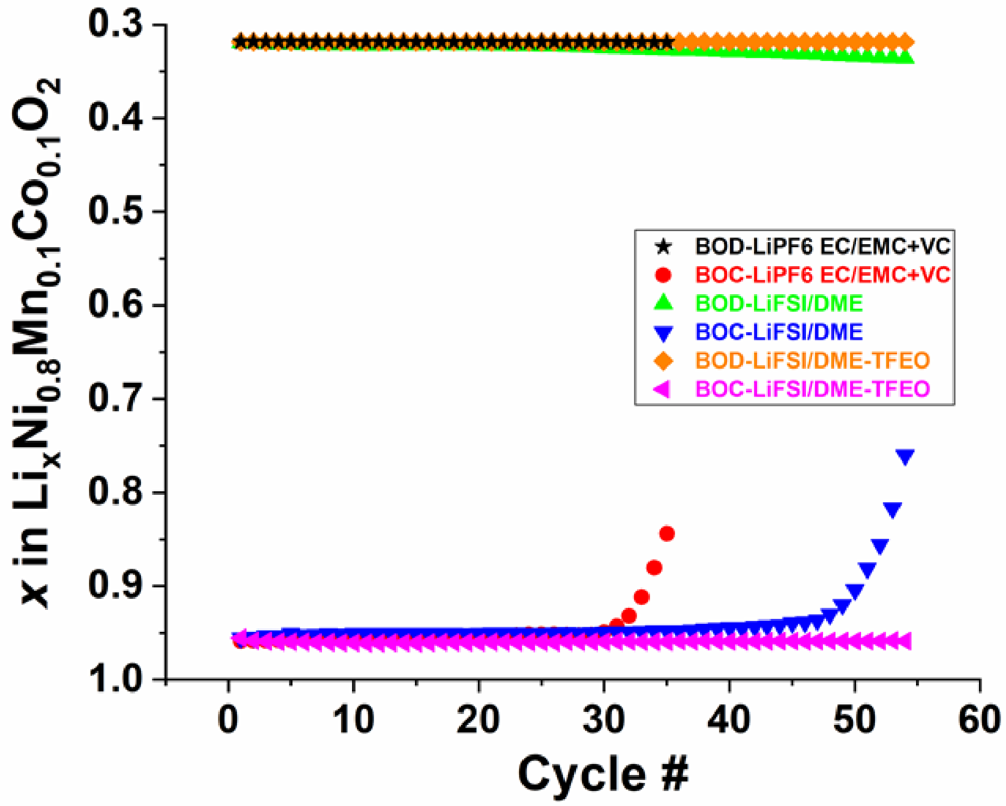
Zhang Y. et al. *J. Electrochem. Soc.* **167**(9), 090502 (2020)

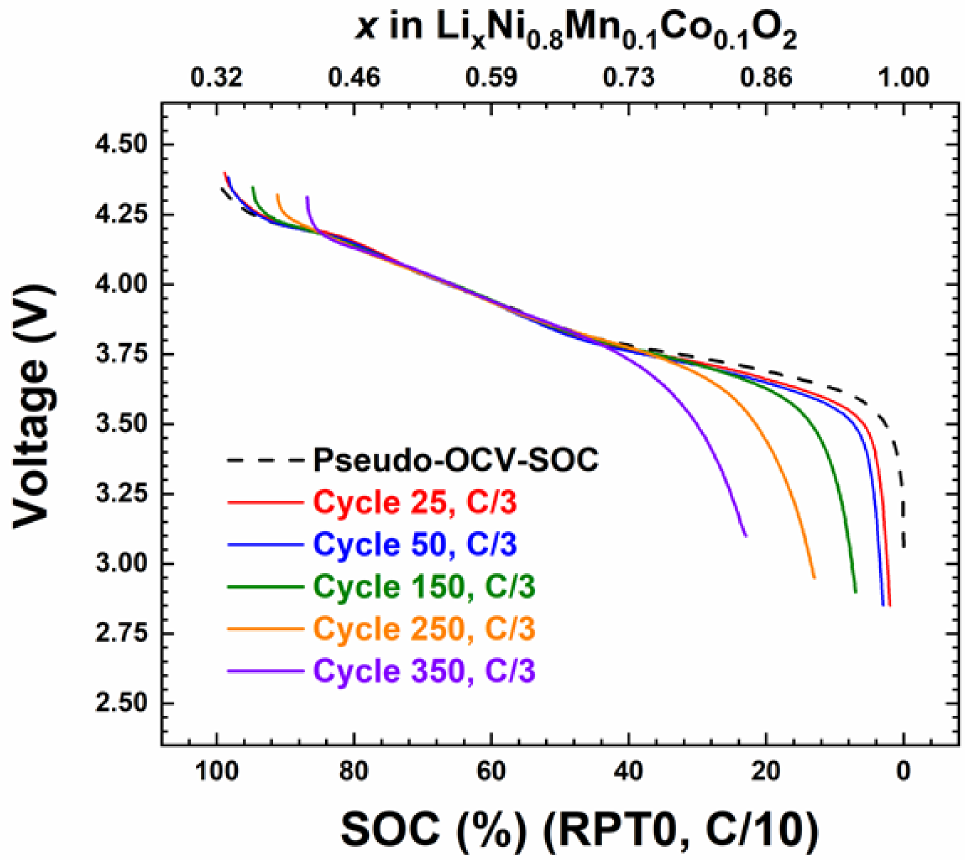
Technical Accomplishments

Li Site Occupancy Variations in Cycle Aging



- Rest voltage showed interfacial stability and impact of LLI
- Electrochemical analytic diagnosis showed Li site occupancy during cycle aging – *Cell kinetic imbalance*



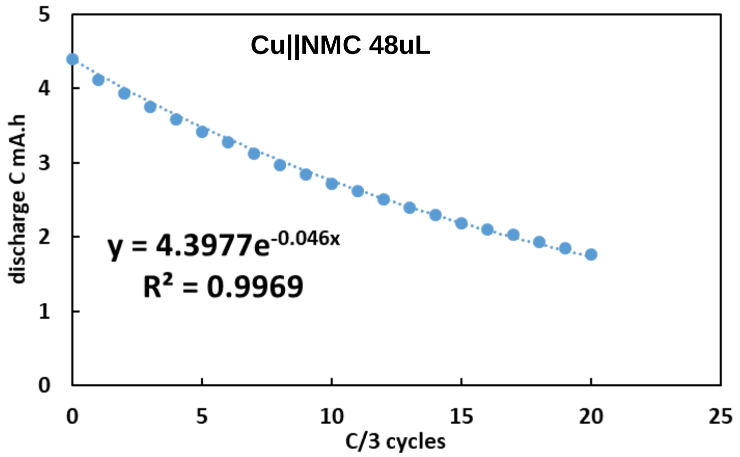


X. Cao et al, *Nature Energy* 4 (2019) 796–805. Zhang Y. et al. *J. Electrochem. Soc.* **167**(9), 090502 (2020)

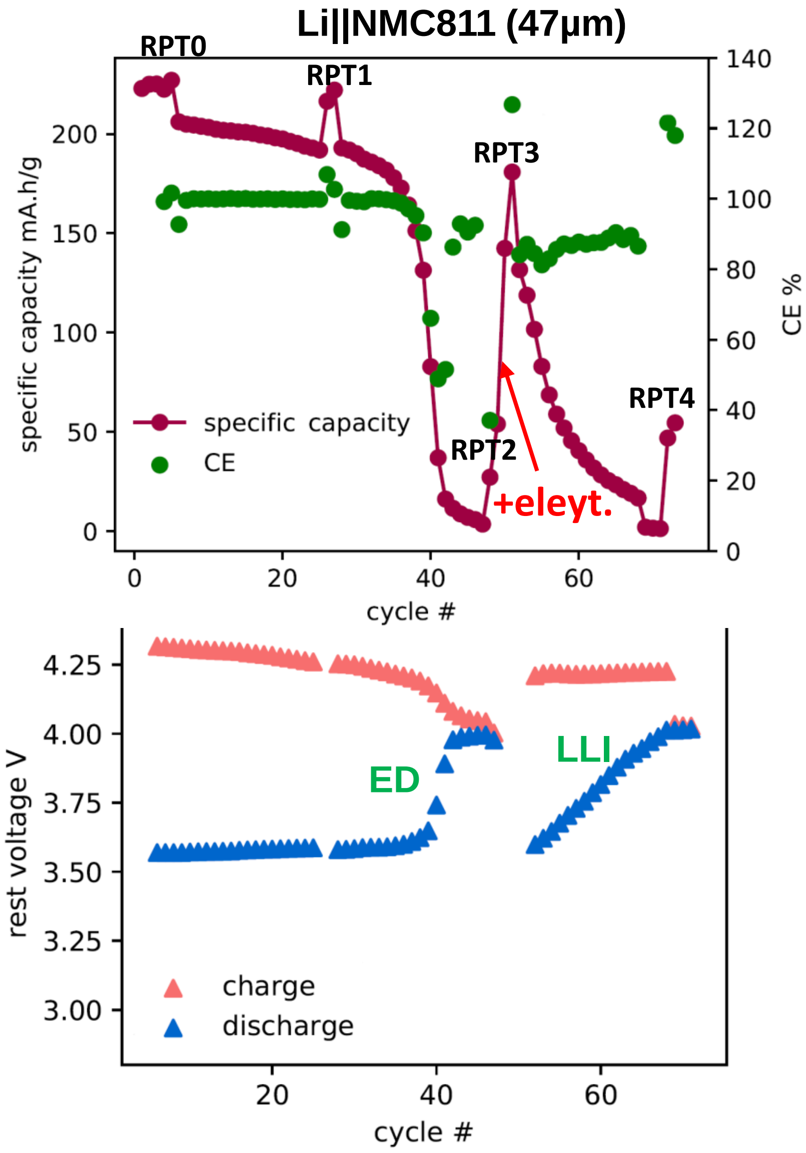
Maximum Lifetime Prediction of Li Metal Cells

- Extraction of loss due to electrolyte depletion vs loss of lithium inventory - *Early validation of technology*

- Extraction of distinct features enables early prediction of maximum expected life based on known cycling procedures



	1.6M flooded	Actual cycles
Li Loss/cycle (excess, Li)	0.951 um	
Predicted cycle (excess)	49	40
Li Loss/cycle (limited, Cu)	4.5%	
Predicted cycle (limited)*	34	18

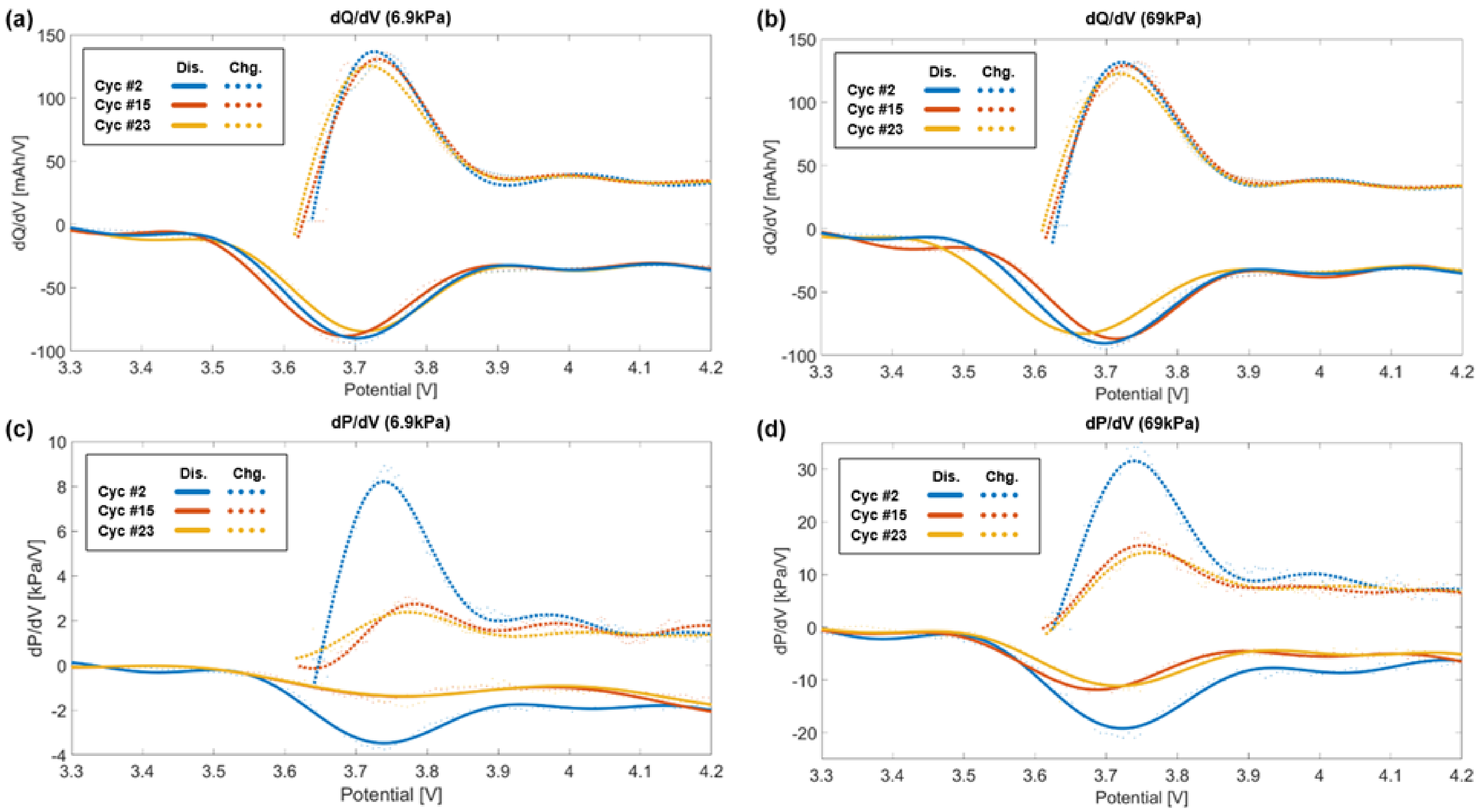


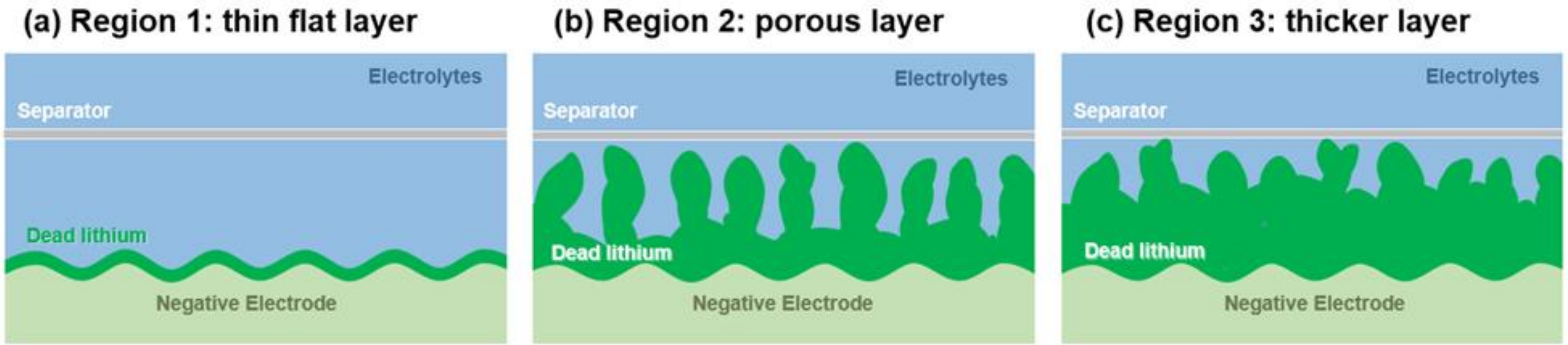
*20% of the capacity retention

Li et. a., patent filed

Technical Accomplishments
Pressure Evolution

- Tracking electrochemical and mechanical response
- Early life dQ/dV and dP/dV track
- Route to understand electrode morphology and full cell mechanical evolution





Raj, A et al, *J. Electrochem. Soc,* **167**, 020511 (2020)
Kim, S et al, *accepted J. Power Sources*

Spatial Resolution Cycled S electrode

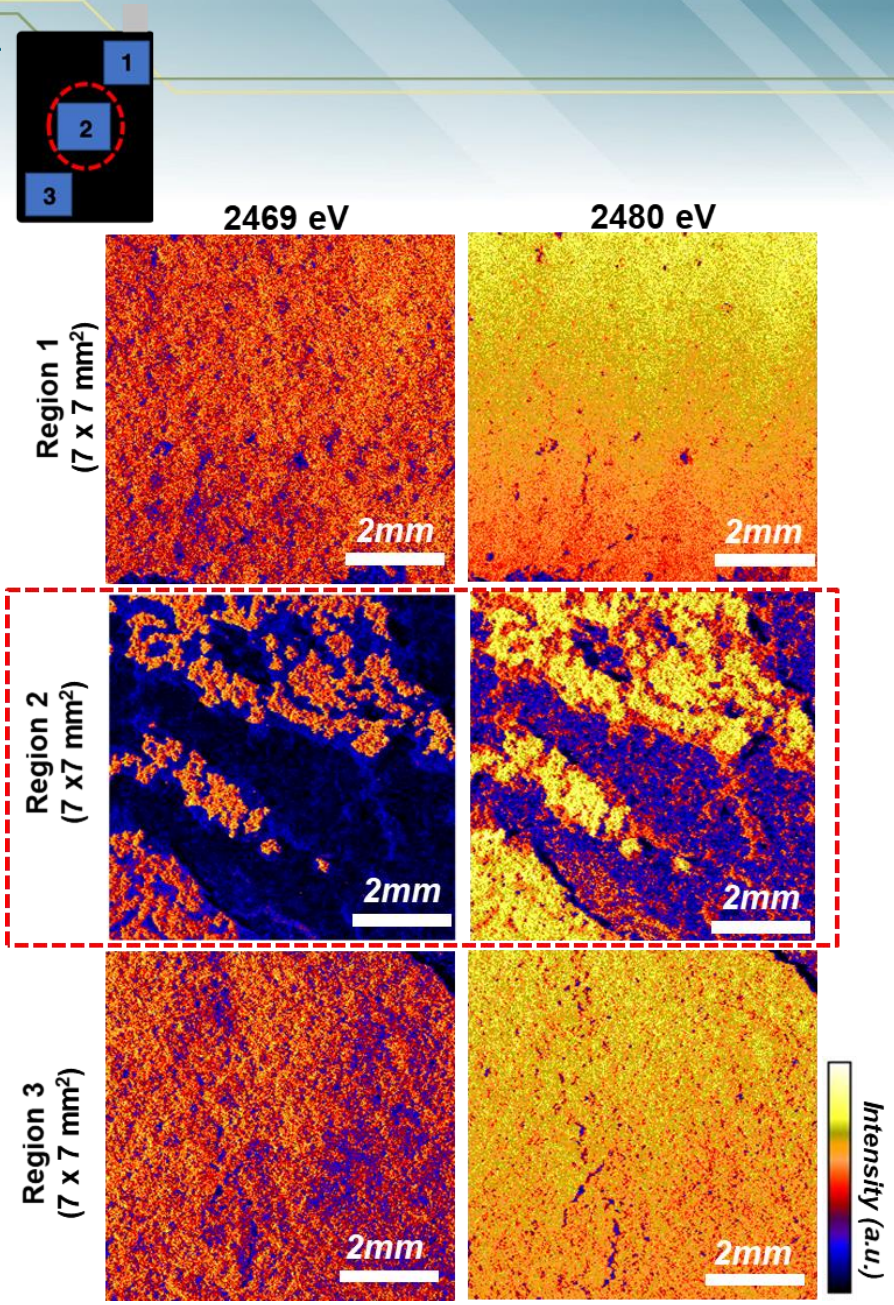
- The area with dark blue color in 2D XRF image indicate the low concentration of sulfur species.

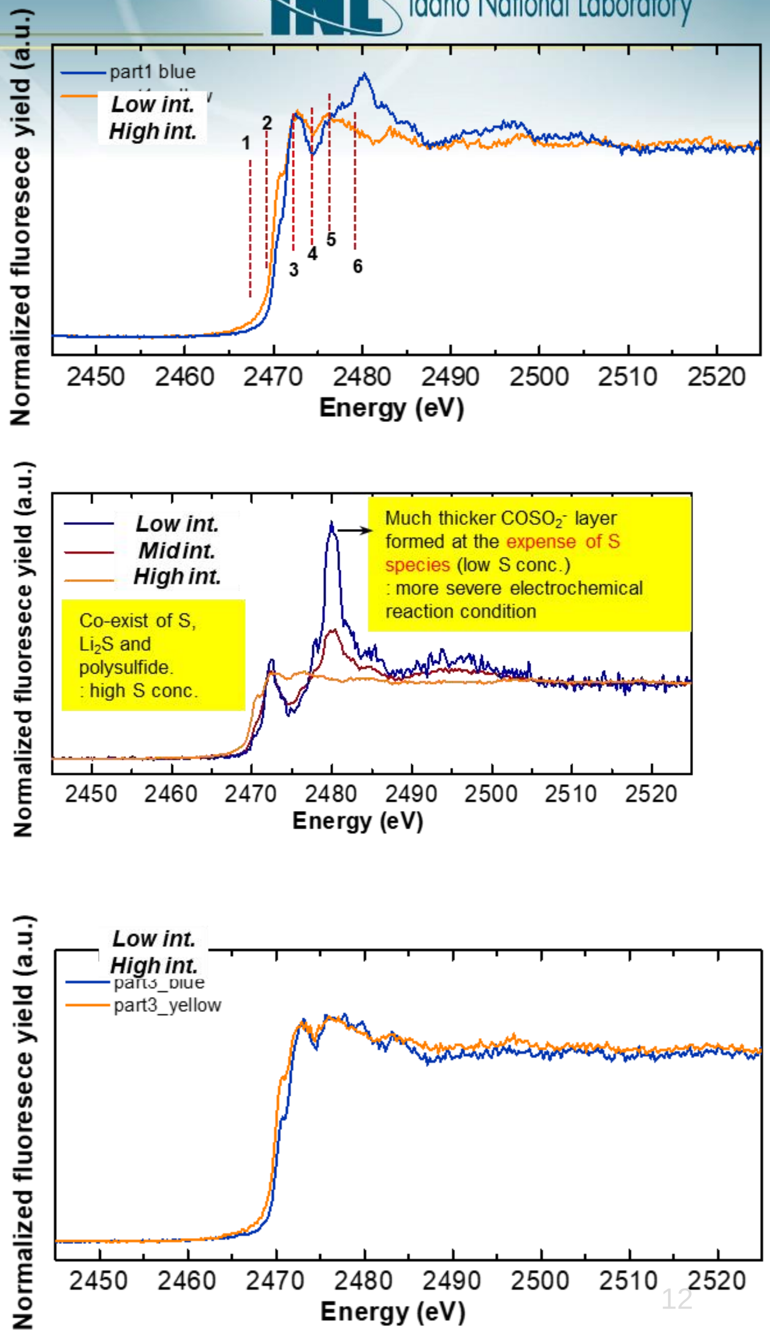
- Relatively, the low sulfur area shows more higher S-O peak. This indicate that elemental sulfur at this area formed more thicker layer of S-O species (insulating CEI layer).

- The area with yellow color indicate the high concentration of poly-sulfide rather than S-O species.

- The region 2 which is a middle part of the electrode shows much heterogeneous chemical distribution.

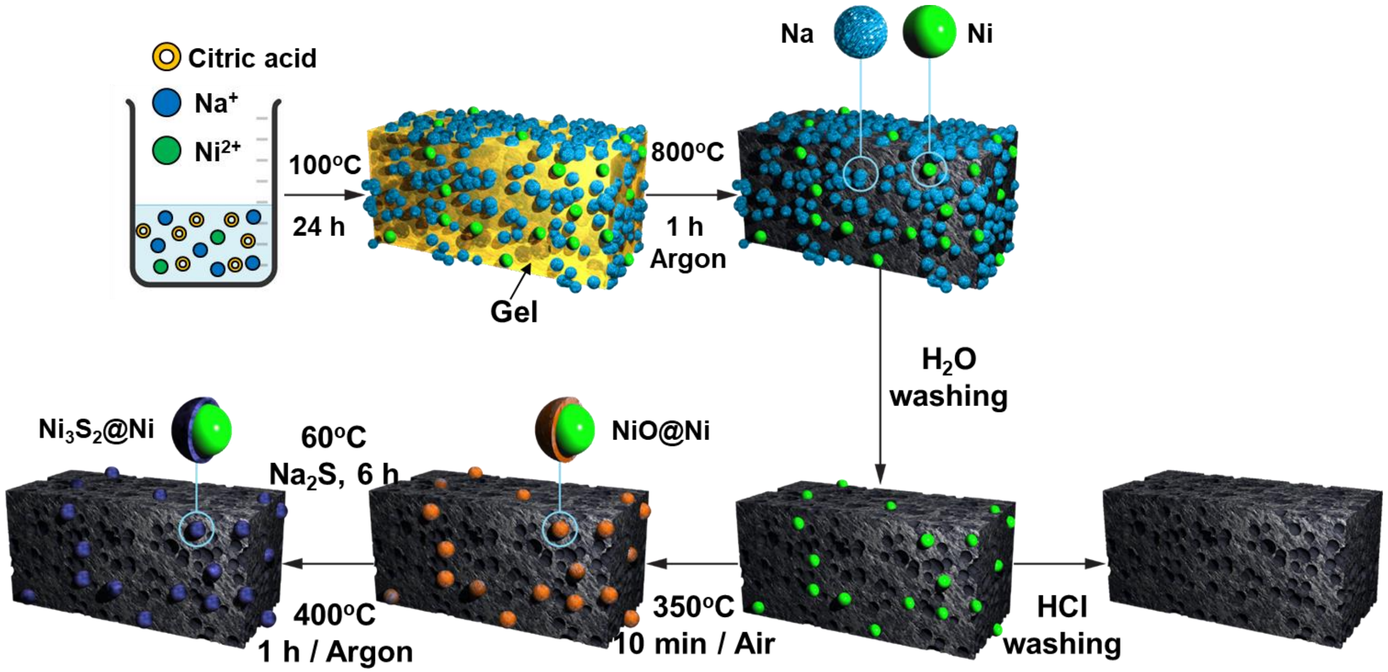
rela
homogeneous





BROOKHAVEN NATIONAL LABORATORY
Pacific Northwest NATIONAL LABORATORY
BATTERY 500 CONSORTIUM
Idaho National Laboratory

Ni-based Core-shell Nanoparticles with Nanoporous Carbon Hybrid Scaffolds

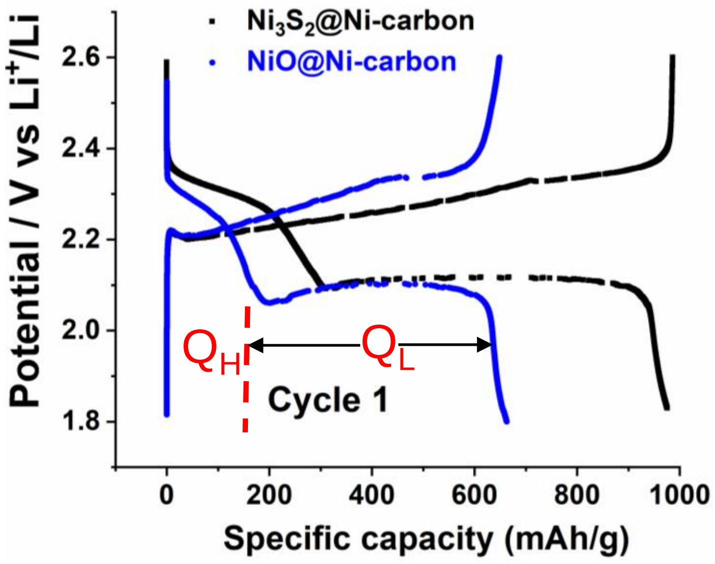


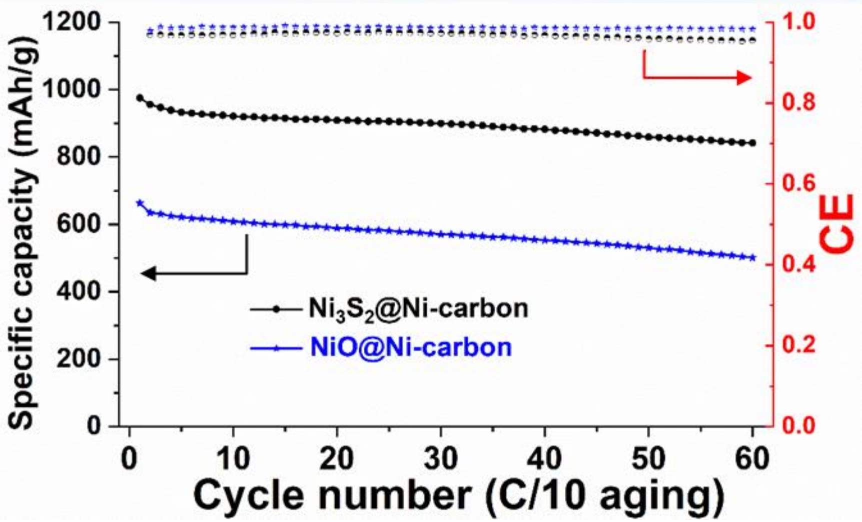
Precursor material	Etching solution	BET surface area [$m^2\ g^{-1}$]
Potassium citrate	HCl	1960
Sodium citrate	HCl	650
KNO_3+ $Ni(NO_3)_2$ + citric acid (mole ratio = 0.9:0.1:1)	HCl	580
	H_2O	314
$NaNO_3$+ $Ni(NO_3)_2$ + citric acid (mole ratio = 0.9:0.1:1)	HCl	252
$NaNO_3$+ $Ni(NO_3)_2$ + citric acid (mole ratio = 1.4:0.1:1)	HCl	328
	H_2O	163

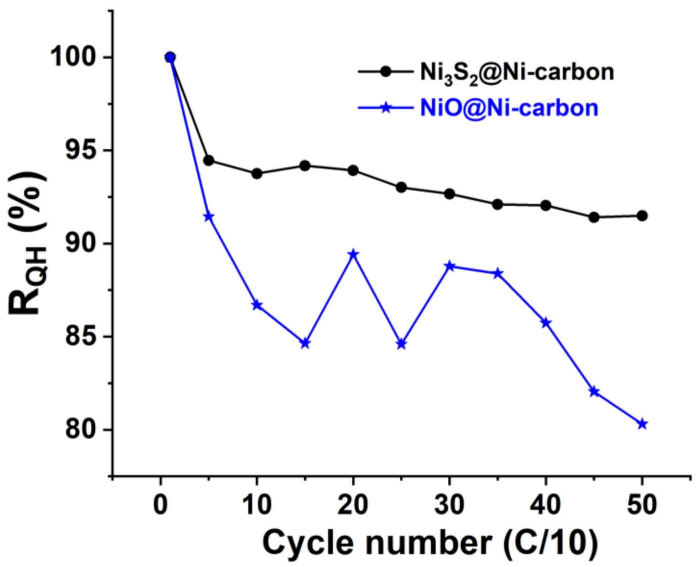
Changing the metal ion and its ratio with citric acid, to tailor surface area of the hybrid materials

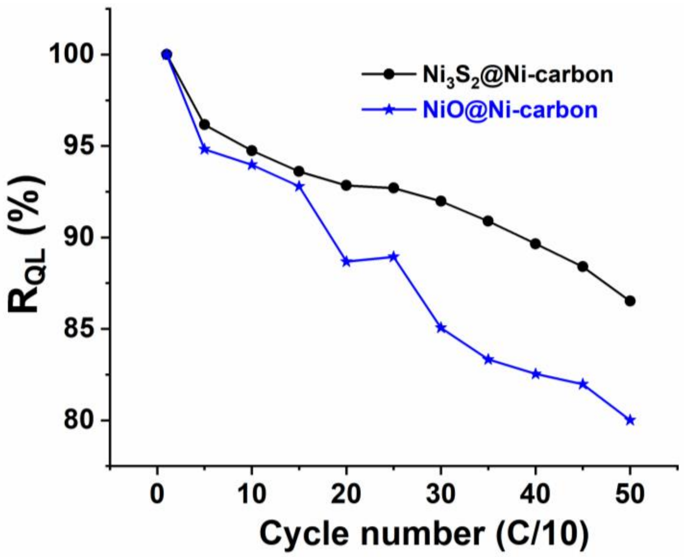
Y. Zhang et. a., submitted

Electrochemical Performance





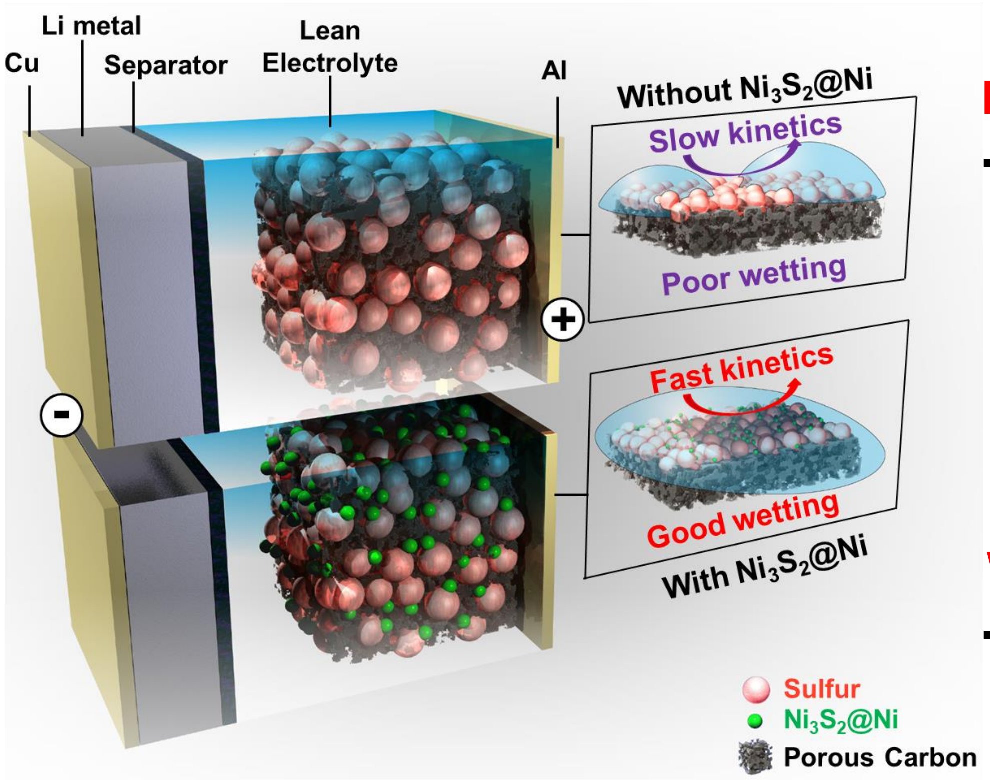




- CE may not tell the full story
- Kinetics and wetting matter for utilization and capacity retention

Y. Zhang et. a., submitted

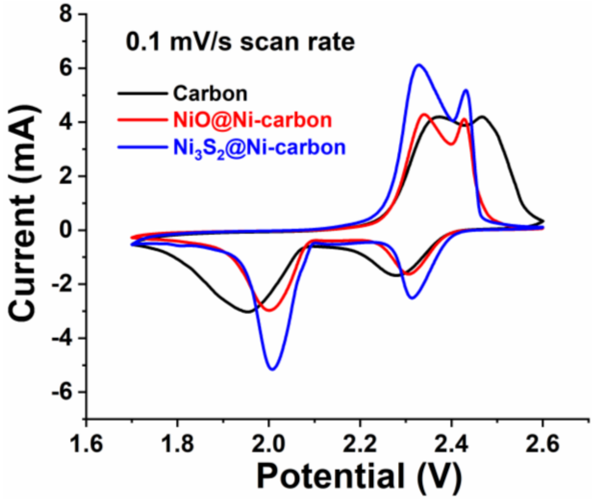
Dual Functions of Ni_3S_2@Ni Core-shell Nanoparticles



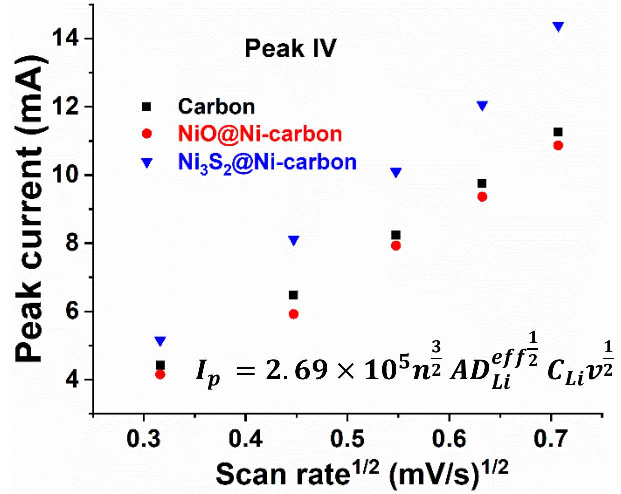
Kinetics

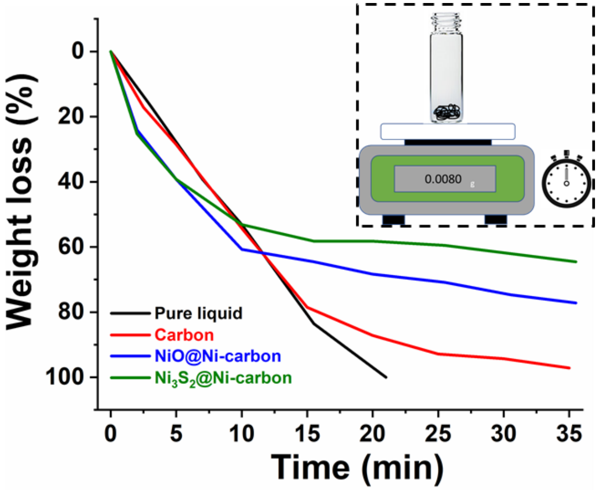
Wetting

Faster kinetics

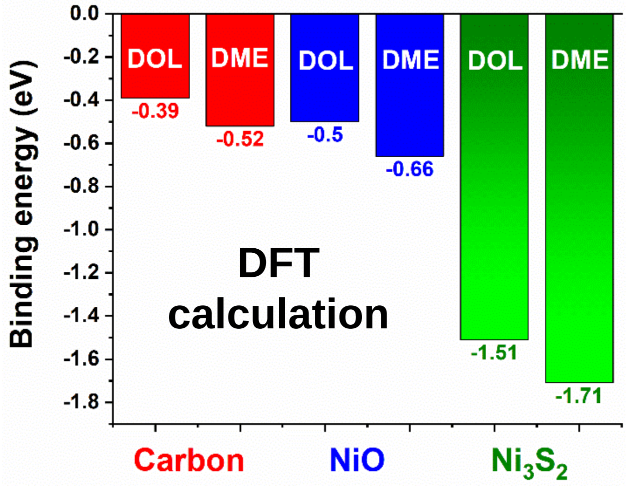


Higher Li^+ diffusion coefficient





Enhanced electrolyte holding



Stronger solvent binding energy

Zhang et. a., submitted

Future Challenges and Plans

- Further understanding coupled electrochemical and mechanical interactions
- Evolving electrochemical analysis for Li-S at the full cell level (Q4 milestone)
- Continued integration of Keystone 1 & 2 advancements especially surface modification
- More directly understanding wetting across life with evolving electrolyte/interfaces
- Expanded demonstration in larger format cells
- Understanding cell performance with varied charging protocols

All activities are subject to future funding

Response to Previous Year Reviewer Comments

- Not reviewed in 2019

Collaboration

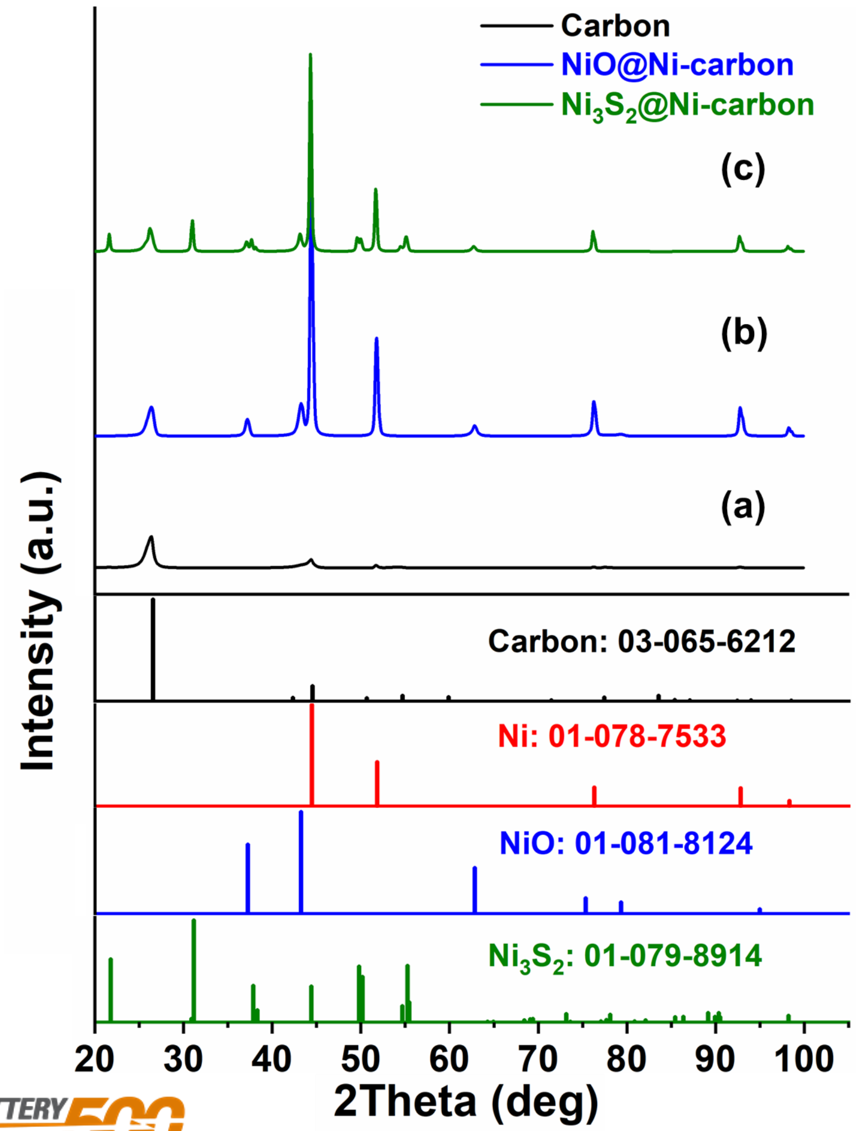
- Core Battery500 Team
- Seedling Battery500 Teams including GM and University of Maryland
- North Carolina State University and Princeton – graduate research associates at INL including coordination with graduate research advisors

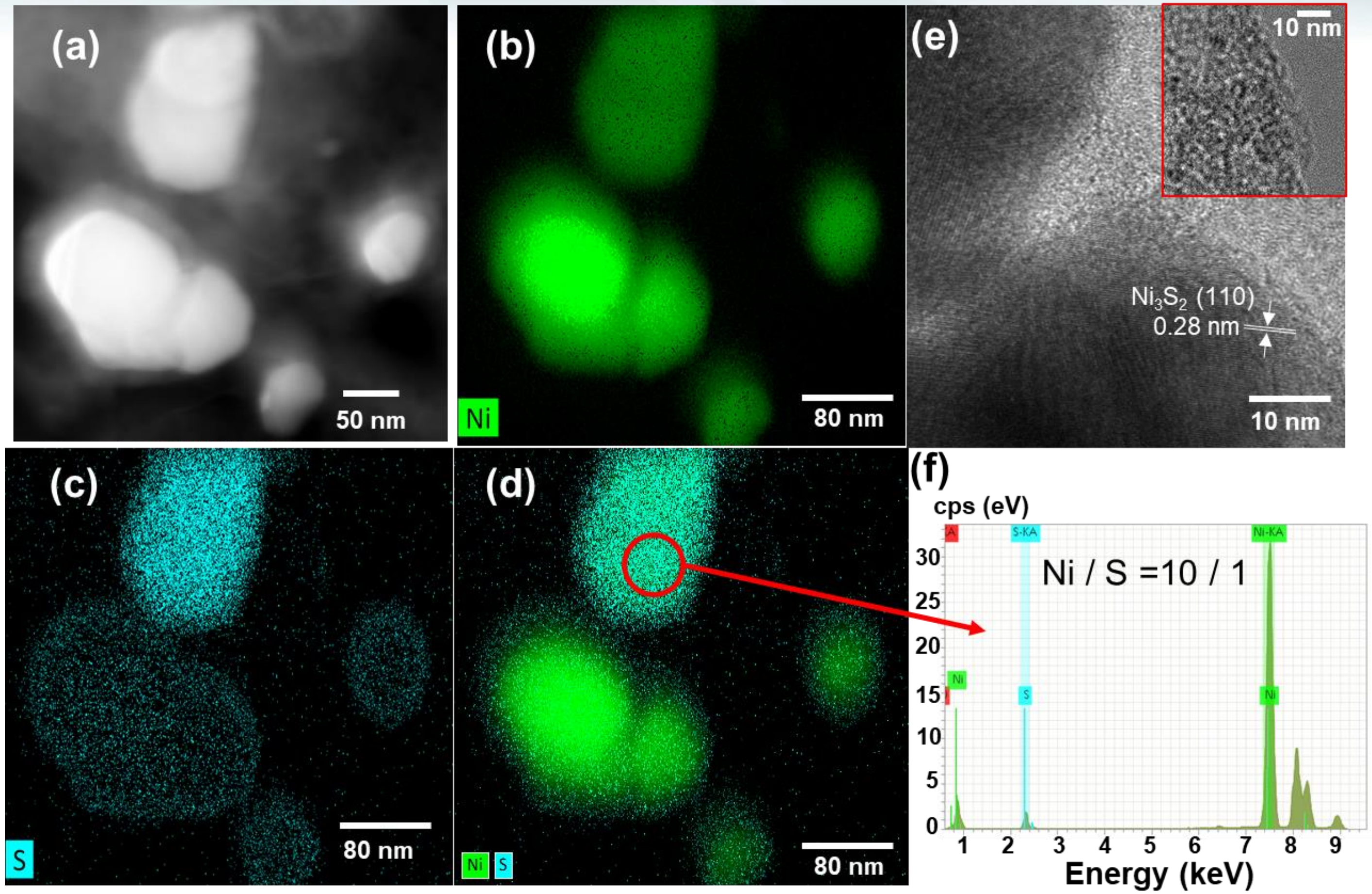
Summary and Acknowledgement

- Demonstrated high cycle life, high energy cell (350 Wh/kg, 250+ cycles)
- Established methods to expand electrochemical analysis of failure for both materials and design
- Expanded analysis and understanding on Li-S including the importance of wetting
- Refined safety information distributed to the broad research community
- *Support from the Vehicle Technologies Office*
- *Staff, post-docs and students at INL, PNNL, UCSD, SUNY-Binghamton, BNL, SLAC, University of Washington, Princeton and NCSU*

Idaho National Laboratory

Material Characterizations

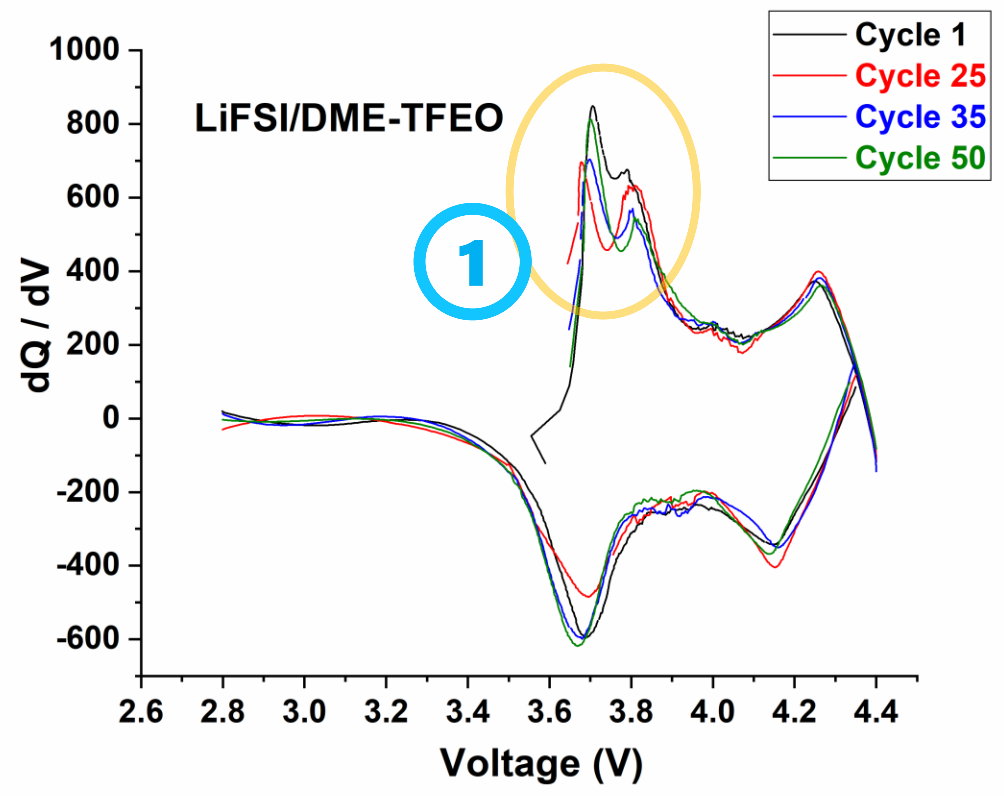


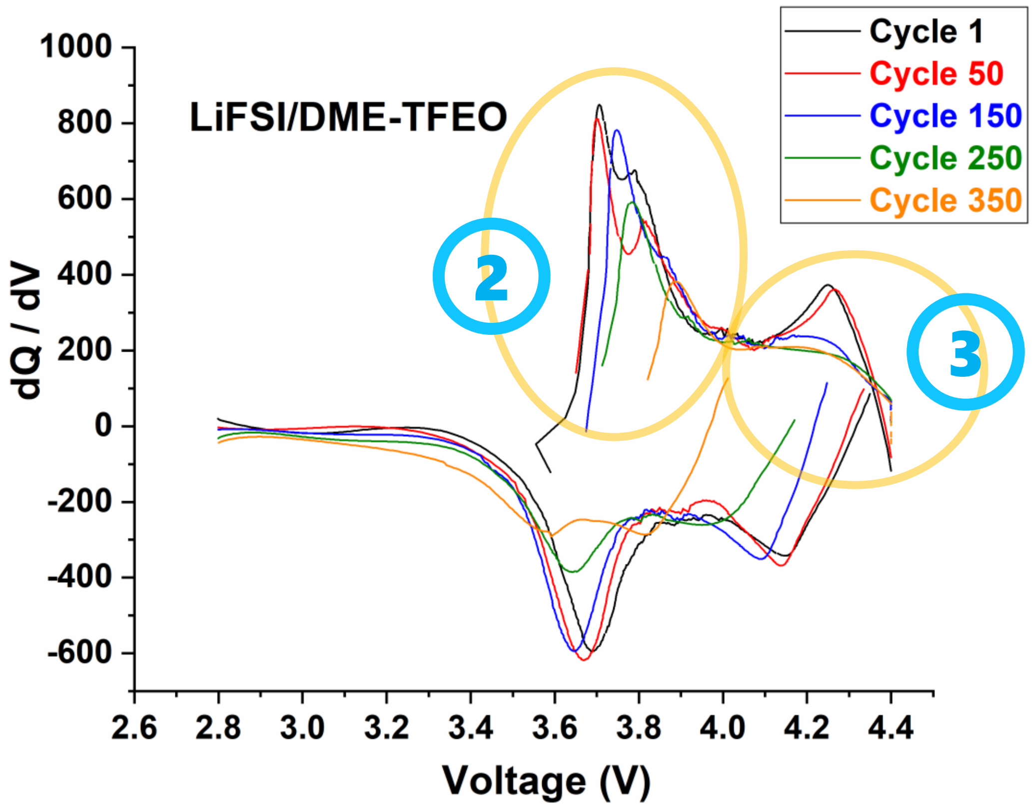


Proving the formation of Ni_3S_2@Ni core-shell nanoparticles on top of porous carbon hosts.

Y. Zhang et. a., submitted

Diagnosis using Incremental Capacity Analysis



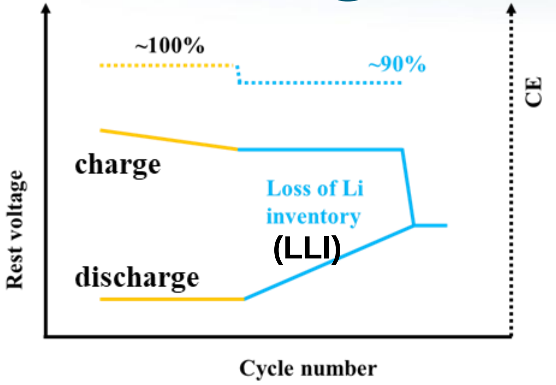


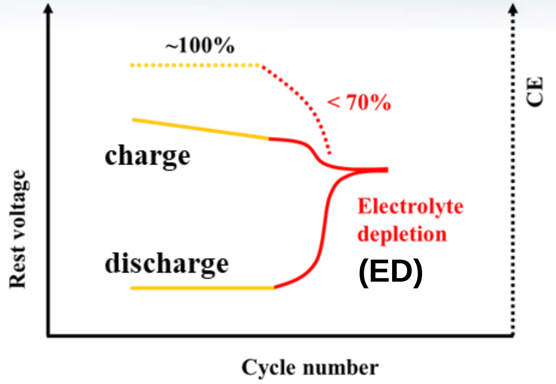
1 Lattice structural changes and phase transition in NMC?

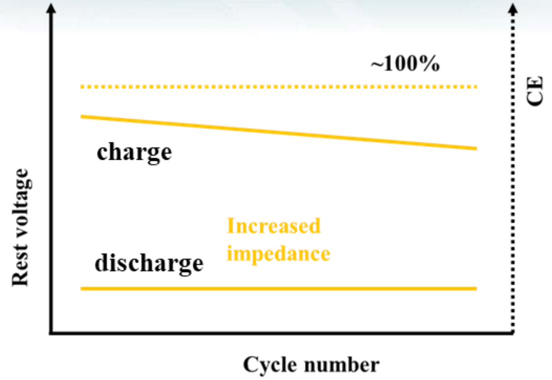
2 Loss of Li Inventory

3 Sluggish site occupation kinetics

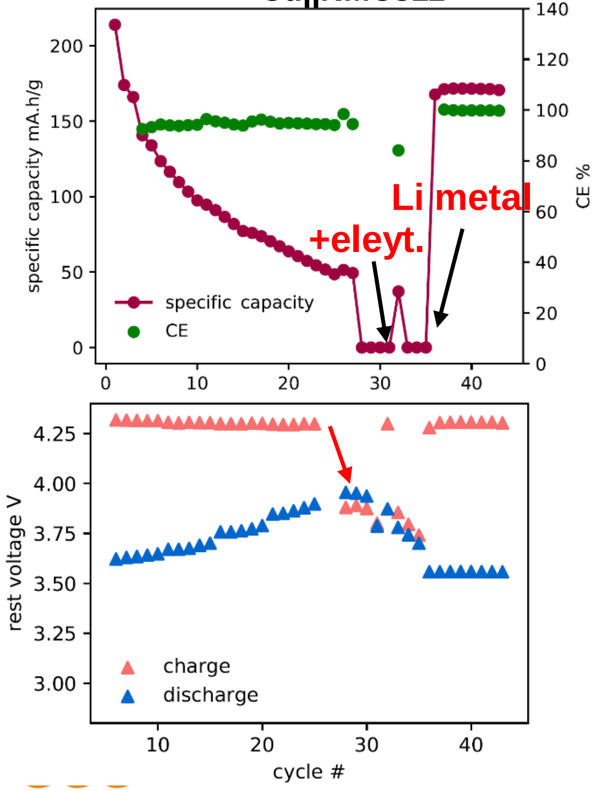
Fast Diagnostics of Failure Mechanisms



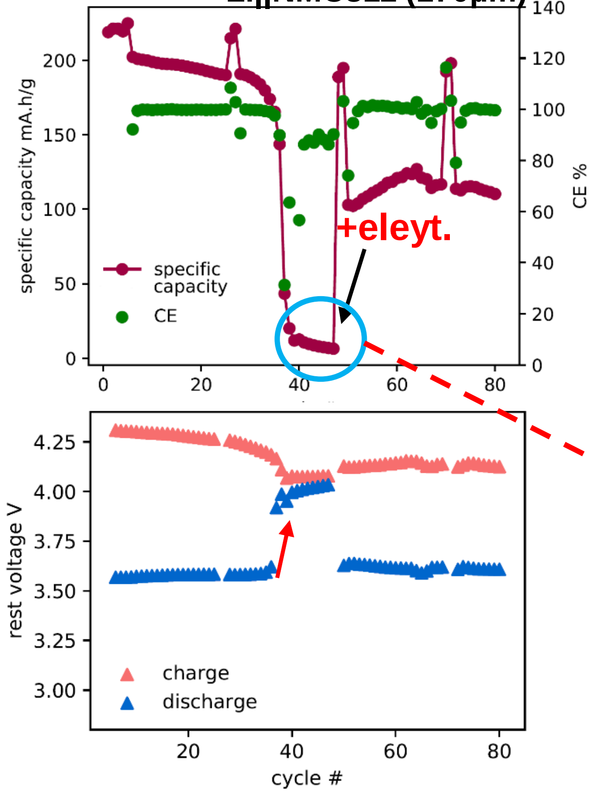




Cu||NMC811



Li||NMC811 (170μm)



- Cells die due to LLI have more dramatic an't be charged. CE becomes lower but remains constant.
- Cells die due to ED can't be discharged. CE continuous decreasing, usually <70%.
- During ED, the local current density increased significantly, causing more SEI and dead Li formed, resulting in high cell impedance in the following recovery cycles.

Publications and Presentations

Selected Publications

- Cell qualification – A performance metric-based approach, Y. Zhang, Q. Wang, B. Liaw, S.C. Nagpure, E.J. Dufek, C.C. Dickerson, *accepted to J. Phys: Energy*
- Correlation of electrochemical and mechanical responses; Differential analysis of rechargeable lithium metal cells, S. Kim et. al, *accepted to J. Power Sources* (2020)
- Pressure evolution in constrained rechargeable lithium-metal pouch cells, A. Raj, C.C. Dickerson, S.C. Nagpure, S. Kim, C. Niu, J. Xiao, B. Liaw and E.J.Dufek, *Journal of the Electrochemical Society,* 167(2020), 020511
- A quantitative failure analysis on Capacity Fade in Rechargeable Lithium Metal Cells, Y. Zhang, B. Liaw, S.C. Nagpure, E. J. Dufek, and C.C. Dickerson, *J. Electrochem Soc*, 167(2020), 090502
- Safety Aspects of Energy Storage Testing", R. Bewley, E.J. Dufek, S.E. Egan, D.K. Jamison, C. Ashton, C.D. Ho, M.C. Evans, T.L Bennett, *J. Electrochem. Soc.*, 166 (2019), E263-E265
- "Pathways for Practical High-Energy Long-cycling Lithium Metal Batteries" Jun Liu et. al, *Nature Energy*, 4 (2019), 180-186
- "Critical Parameters for Evaluating Coin Cells and Pouch Cells of Rechargeable Li-metal Batteries" Shuru Chen, et. al., *Joule*, 3 (2019), 1094-1105.
- "Implications of Local Current Density Variations on Lithium Plating Affected by Cathode Particle Size" A. W. Abboud, E.J.Dufek, B.Y. Liaw, *J. Electrochem. Soc.*, 166 (2019), A667-A669.